solution was cooled to −35° and was flushed with nitrogen. Fluorine–nitrogen, 1:9, was passed over the stirred mixture at 20 ml/min for 4 hr while the temperature was allowed to rise slowly to −5°. During the fluorination the mixture formed two phases; the upper phase was methanol and was discarded. The lower phase contained 1,1-bis(difluoramino)heptafluorobutyl methyl ether (**6**) in CCl$_4$. **6** was separated by preparative glpc using a 20 ft × $^3/_8$ in. column (15% SE-30 on 60–80 mesh Chromosorb P) at 100° to give 0.54 g of pure product; bp 25° (25 mm), n^{28}_{D} 1.3088; ir (gas) 3.35 (w) CH; 6.90 (w), 7.50 (w); 8.10 (s) CF; 8.82 (m) COC; 10.25 (m), 10.45 (m), 11.18 (m) and 11.70 (m) NF$_2$; 12.50 μ (m); nmr (CCl$_4$) τ 5.95 (s, 3, CH$_3$), φ^* −21.8 (s, 4, NF$_2$), 81.6 (t, 3, J = 12, CF$_3$), 115.5 (m, 2, CF$_2$CO), 125.2 (m, 2, CF$_3$CF$_2$).

Anal. Calcd for $C_5H_3F_{11}N_2O$: C, 19.00; H, 0.95; N, 8.87. Found: C, 19.48; H, 0.85; N, 8.63.

N,N,N′-Trifluorodifluoronitroacetamidine (5).—A 2.5-g sample (0.014 mol) of powdered difluoronitroacetamidine hydrochloride[15] was mixed thoroughly with 7.5 g of powdered sodium fluoride. The mixture was placed in a U tube in alternating layers with glass wool, and the tube was cooled in an ice water bath. The tube was flushed with nitrogen, and a 1:9 mixture of fluorine–nitrogen was passed through the U tube at 20 ml/min for 6 hr. The condensable exit gases were collected in a 0° trap and a −78° trap; the contents of the 0° trap was mainly water and was discarded. The −78° trap contained 1.2 g of a clear colorless liquid consisting of five compounds in almost equal amounts, but only one isomer of **5** was evident. **5** was isolated by preparative glpc using a 20 ft × $^3/_8$ in. column (15% Kel-F oil on 60–80 mesh Chromosorb P) at 40°. One of the other five compounds was also isolated and identified as difluoronitroacetonitrile by comparison of its ir spectrum with that of a known sample:[15] bp of **5** *ca.* 20°; ir (gas) 6.18 (s), 7.45 (m), 7.62 (m), and 12.25 (m) NO$_2$; 8.05 (s) CF; 8.70 (m), 9.60 (w); 10.10 (s), 10.70 (s), and 11.15 μ (m) NF; nmr (CDCl$_3$) φ^* −45.0 (s, 2, NF$_2$), −42.7 (s, 1, C=NF), 86.1 (quintet, 2, J = 10 Hz, CF$_2$).

1,1-Bis(difluoramino)-2,2-difluoro-2-nitroethyl Methyl Ether (7). (a) Addition of Methanol to 5.—A 0.5-g sample (2.6 mmol) of **5** dissolved in 3 ml of acetonitrile was placed in a glass reactor equipped with Teflon needle valves and a magnetic stirring bar. Methanol (0.4 g, 12.5 mmol) was added to the solution at 0°, the reactor was sealed, and the reaction mixture was allowed to stir at 0° for 4 hr. Nmr analysis of the mixture confirmed the presence of the methanol adduct, 1-fluoramino-1-difluoramino-2,2-difluoro-2-nitroethyl methyl ether (**5a**), and showed that reaction was essentially complete; nmr (CH$_3$CN–CH$_3$OH), φ^* −19.8 (s, 2, NF$_2$), 92.0 (broad t, CF$_2$), 143.1 (d of heptets, J = 49.7 and 6.5 Hz, NFH).

(b) **Fluorination of 5a.**—Since **5a** could not be isolated from the reaction mixture, the fluorination step was carried out *in situ*. The acetonitrile reaction mixture was cooled to −35°, the system was purged with nitrogen, and a mixture of 1:3 fluorine–nitrogen was passed over the stirred reaction mixture at 20 ml/min for 2 hr. The reaction mixture was warmed to ambient temperature, and the volatile products were collected in a −35° trap by vacuum transfer at 0.3 mm. Analysis of the condensate by glpc showed equivalent amounts of three main products in a large amount of acetonitrile. The three products were isolated by glpc using a 5 ft × 0.25 in. column (20% SE-30 on 80–100 mesh Chromosorb P) at 80°. In the order of increasing retention time, the compounds were identified by ir and nmr. **9**, methyl difluoronitroacetate: nmr (CCl$_4$) τ 5.93 (s, 3, CH$_3$), φ^* 93.4 (t, 2, J = 9.8 Hz, CF$_2$); ir (neat) 3.48 (w), 6.98 (m), 7.55 (s), 9.80 (s), and 10.75 (m) CH; 5.61 (s) C=O; 6.28 (s) and 12.50 (s) NO$_2$; 8.10 (m), 8.35 (s), and 8.60 (s) CF; 11.82 μ (m). The ir and nmr spectra of this compound were identical with the spectra of a sample prepared by a previously reported method.[26]

8, methyl 2,2-difluoro-2-nitrofluoriminoacetate: nmr (CCl$_4$) φ^* 40.0 (s, 1, C=NF), 92.5 (t, 2, J = 8.5 Hz, CF$_2$); ir (neat) 3.48 (w), 6.90 (m), 7.35 (m), 7.50 (s), and 9.72 (s) CH; 6.05 (s) C=N; 6.28 (s) and 12.35 (s) NO$_2$; 8.10 (s), 8.38 (s), and 8.52 (s) CF; 9.38 (m) COC; 10.40 (m) and 11.20 μ (s) NF.

7, 1,1-bis(difluoramino)-2,2-difluoro-2-nitroethyl methyl ether: nmr (CCl$_4$) φ^* −21.9 (s, 4, NF$_2$), 90.4 (quintet, 2, J = 12.1 Hz, CF$_2$); ir (neat) 3.38 (w), 7.91 (m), and 7.48 (m) CH; 6.25 (s) and 12.18 (s) NO$_2$; 8.00 (s), 8.18 (s), and 8.50 (s) CF; 9.10 (m) COC; 10.60 (s), 11.25 μ (s) NF.

Registry No.—**1** (*syn*), 21372-60-1; **1** (*anti*), 21372-59-8; **2** (*syn*),25238-00-0; **2** (*anti*), 25238-01-1; **3** (*syn*), 25238-02-2; **3** (*anti*), 25238-03-3; **4**, 25356-05-2; **4a**, 25238-04-4; **5**, 25238-05-5; **5a**, 25238-06-6; **6**, 25238-07-7; **7**, 25238-08-8; **8**, 25238-09-9.

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Synthesis and Cycloaddition Reactions of Dehydrohydantoins

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Several $\Delta^{1,5}$-imidazoline-2,5-diones (dehydrohydantoins) have been prepared and their chemistry has been examined. They are active Diels–Alder dienophiles and also react with monoolefins (ene reaction) and nucleophiles (addition across the >C=N– bond). The reactivity of the dehydrohydantoins (I) depends markedly on the substituent in the 5 position with 5-H > 5-CO$_2$Me > 5-Ph. The dienophilic activity of the dehydrohydantoins appears to be intermediate between those of the corresponding α-dicarbonyl azo compounds and the α-diacyl olefins. The spectra of 5-phenyl-3-methyldehydrohydantoin (Ib), which is isolable and atmospherically stable, indicate that it is a cross-conjugated system similar to 3-phenylmaleimide.

In the course of studies of the Diels–Alder reaction,[1] we have made extensive use of α-dicarbonyl azo compounds, RCON=NCOR, as dienophiles. These azo compounds are three or four orders of magnitude more reactive than the corresponding olefins,[2] and the cyclic examples such as 4-phenyl-1,2,4-triazoline-3,5-dione[2d] are among the most active dienophiles known. The reasons for the remarkable reactivity of these α-dicarbonyl azo compounds are not known. Geometric factors and polarizability are certainly important; however, we suspect that the energetics of transforming an azo ester linkage into two C–N bonds and an unusually strong N–N bond[3] may also be highly favorable.

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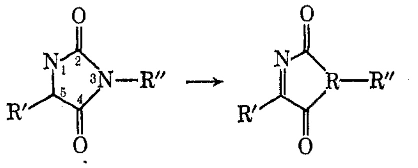
(1) (a) A. B. Evnin and D. R. Arnold, *J. Amer. Chem. Soc.*, **90**, 5330 (1968); (b) A. B. Evnin, R. D. Miller, and G. Evanega, *Tetrahedron Lett.*, 5863 (1968); (c) A. B. Evnin, A. Lam, J. Maher, and J. Blyskal, *ibid.*, 4497 (1969).

(2) (a) J. Sauer and B. Schröder, *Angew. Chem., Int. Ed. Engl.*, **4**, 711 (1965); (b) J. Sauer, *ibid.*, **6**, 16 (1967); (c) J. Sauer and B. Schröder, *Chem. Ber.*, **100**, 678 (1967); (d) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).

(3) The dissociation energy of the N–N bond in N,N-diacylhydrazines is probably >50 kcal: E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropulos, and L. M. Kyle, *J. Amer. Chem. Soc.*, **89**, 4875 (1967).

Considerations of the differences between the azo compounds and the olefins led us to an interest in the dienophilic properties of the intermediate α-diacylimines, $RCOCR'{=}NCOR$.[4] This class of compounds was the more intriguing since no examples were, as yet, reported in the literature.[5]

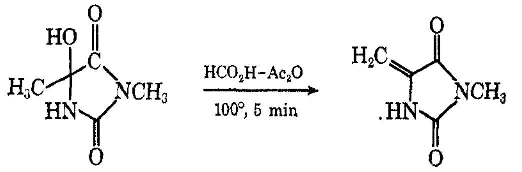
We decided upon the $\Delta^{1,5}$-imidazoline-2,5-diones (dehydrohydantoins) (I) as the starting point of this investigation. The choice was dictated by the ready availability of the precursor hydantoins (II) and by the extensive data available on the analogous C=C and N=N systems, maleimides and 1,2,4-triazoline-3,5-diones, respectively.



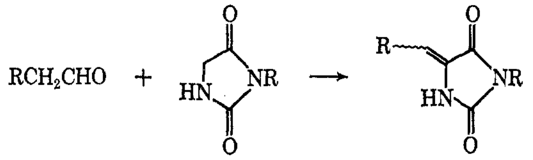
II I

Results

Synthesis and Properties of Dehydrohydantoins.—The literature on hydantoin chemistry indicated that several approaches, which could have given 5-substituted dehydrohydantoins, resulted instead in the formation of the *exo*-methylene tautomers[6-8] (eq 1[6] and 2[8]). We accordingly chose only systems incapable of undergoing such an isomerization.



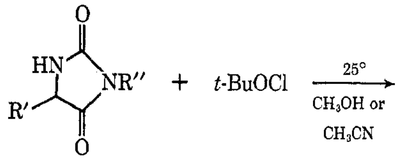
(1)



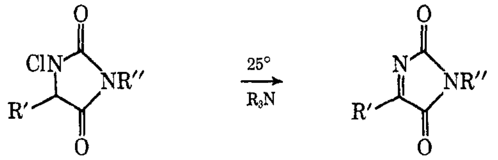
(2)

Two routes were considered for conversion of hydantoins to the corresponding dehydro form: oxidative dehydrogenation and substitution (*e.g.*, halogenation) followed by elimination. After some abortive attempts at oxidation, a halogenation–dehydrohalogenation route was developed.[9]

Treatment of the hydantoins IIa–c with *t*-butyl hypochlorite in methanol gave the N-chloro compounds III in quantitative yield. The reaction could be followed by nmr or ir spectroscopy; the N–H stretching absorptions at 3450 and 3250 cm^{-1} are especially convenient indicators of the extent of reaction. Alcoholic solvents were required for the chlorination of IIa and IIb, since there was no reaction in aprotic media;[10] IIc, however, reacted readily with *t*-butyl hypochlorite in acetonitrile.



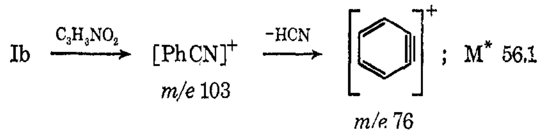
IIa, R' = H; R'' = CH$_3$
b, R' = Ph; R'' = CH$_3$
c, R' = CO$_2$Me; R'' = CH$_2$Ph



IIIa, R' = H; R'' = CH$_3$
b, R' = Ph; R'' = CH$_3$
c, R' = CO$_2$Me; R'' = CH$_2$Ph

Ia, R' = H; R'' = CH$_3$
b, R' = Ph; R'' = CH$_3$
c, R' = CO$_2$Me; R'' = CH$_2$Ph

Reaction of these N-chloro compounds (IIIa–c) with triethylamine, tetramethylethylenediamine, or 1,5-diazabicyclo[5.4.0]undec-5-ene[11] resulted in elimination of hydrogen chloride and the formation of the dehydrohydantoins Ia–c. Evidence for the formation of the dehydrohydantoins was the precipitation of the amine hydrochloride, the formation of 1,4-adducts with dienes, and, in the case of IIIb, the properties of the isolated product, Ib. All of the dehydrohydantoins are sensitive to moist air and are preferentially handled in an inert atmosphere.



5-Phenyl-3-methyldehydrohydantoin (Ib) was isolated by sublimation [60° (0.02 mm)]. It is a crystalline, yellow compound, mp 148–150°, with substantial atmospheric stability, once purified. The nmr spectrum (CDCl$_3$) shows only N-methyl and aryl hydrogens. The mass spectrum (70 ev) has a base peak at *m/e* 103 (PhCN) and prominent fragments at *m/e* 131 (M − 57, CH$_3$NCO) and *m/e* 76, in addition to a strong parent peak at *m/e* 188. The important fragment at *m/e* 76 is of interest since it is almost certainly benzyne. The presence of a metastable at *m/e* 56.1 relates this fragment to *m/e* 103 (PhCN). In the mass spectrum of benzonitrile (70 eV), *m/e* 76 is the most important fragment ion.[12] The absorption spectrum of Ic contains maxima at 284 and 325 nm, and the infrared spectrum

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(4) In a recent review of heterodienes and heterodienophiles there was only one reference to acylimines and no examples of cyclic systems: J. Hamer, Ed., "1,4-Cycloaddition Reactions," Vol. 1, Academic Press, London, 1967, p 128.

(5) (a) After the completion of this work, a study of the apparent *in situ* generation of Ia was reported: E. Goldstein and D. Ben-Ishai, *Tetrahedron Lett.*, 2631 (1969). (b) Very recently, the preparation of 3-phenyl-2-azanaphthoquinone was reported: I. Felner and K. Schenker, *Helv. Chim. Acta*, **52**, 1810 (1969).

(6) S. Murahashi, H. Yuki, K. Kosai, and F. Doura, *Bull. Chem. Soc. Jap.*, **39**, 1559 (1966).

(7) E. J. McMullen, H. R. Henze, and R. W. Wyatt, *J. Amer. Chem. Soc.*, **76**, 5636 (1954).

(8) T. B. Johnson, *ibid.*, **61**, 2485 (1939).

(9) The conversion of PhCH(CN)NHCOPh to PhC(CN)=NCOPh by SOCl$_2$ in pyridine has been reported. The authors describe the reaction as an oxidation although it must involve chlorination and dehydrochlorination steps: M. Fujimori, E. Haruki, and E. Imoto, *Bull. Chem. Soc. Jap.*, **41**, 1372 (1968).

(10) Most amides can be chlorinated using *t*-BuOCl in nonpolar solvents: R. S. Neale, N. L. Marcus, and R. G. Schepers, *J. Amer. Chem. Soc.*, **88**, 3051 (1966).

(11) H. Oediger, H-J. Kabbe, F. Möller, and K. Eiter, *Chem. Ber.*, **99**, 2012 (1966).

(12) A. Cornu and R. Massot, "Compilation of Mass Spectral Data," Heydon and Son, Ltd., London, England, 1966, p 37c.

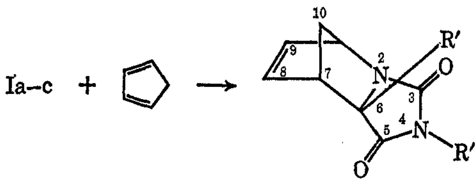
has a characteristic intense doublet at 1590 and 1563 cm^{-1}. The dehydrohydantoins Ic and Ia could not be isolated because of their instability in the atmosphere; however, they could be generated and utilized *in situ*.

Reactions of Dehydrohydantoins.—The dehydrohydantoins Ia–c are active dienophiles and undergo 4 + 2 cycloadditions under mild conditions even with dienes of modest activity. The reactivity of the dehydrohydantoin depends markedly on the substituent in the 5 position with Ic $\gg$ Ib. The 5-phenyl compound, Ib, reacted rapidly with cyclopentadiene and 1-methoxybutadiene and slowly with isoprene and cyclohexadiene at 25°. There was no reaction with furan or 3,5-diphenyl-4,4-dimethylisopyrazole even at 75°. Competitive experiments showed that it was substantially less reactive than N-phenylmaleimide with 2,3-dimethylbutadiene. Comparison with data in the literature suggests, however, that its reactivity is probably greater than that of phenylmaleic anhydride.[13] In contrast to Ib, Ic reacted within minutes with 1-methoxybutadiene ($k > 0.01$ l. mol^{-1} sec^{-1}), cyclohexadiene, or isoprene at 25°. The parent dehydrohydantoin, Ia, undergoes side reactions under our conditions so that yields of cycloadducts are low and irreproducible, and rates of reactions are difficult to estimate. In the reaction of its precursor IIIa, with bases, decomposition by pathways other than those leading to Ia may be important.

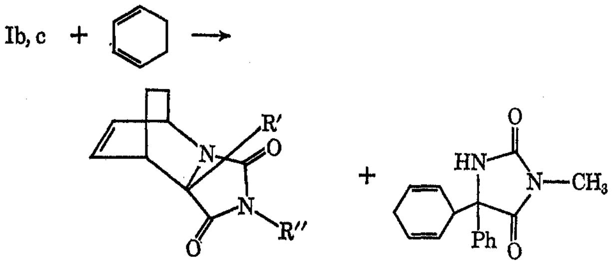
Only one cycloadduct was obtained by reaction of cyclopentadiene with Ia, Ib, or Ic; a second stereoisomer would have been detectable (by nmr) at concentrations of >5%. The stereochemistry of the adduct IVa was assigned by comparison of the 6-H coupling constant with those observed in analogous norbornene derivatives. In the spectra of IVa ($CDCl_3$) this proton appears as a doublet, $J = 3$ Hz, at δ 4.28. In norbornene derivatives the coupling between bridgehead and *exo* protons is 3–5 Hz and that between bridgehead and *endo* protons is approximately 0.[14] The cycloadducts IVb and IVc are assumed to have *endo* stereochemistry by analogy to IVa and to the adduct of cyclopentadiene and phenylmaleic anhydride, whose configuration was unambiguously established as *endo*.[15]

Reactions of either Ib or Ic with 1-methoxybutadiene were rapid and afforded high yields, 70–85% (isolated), of the adducts VIIIb and VIIIc, respectively. None of the positionally isomeric adducts, IXb and IXc, could be detected, although 5% could have been missed. Structural assignments are based on nmr spectroscopy. The spectra of both compounds show an AB pattern (2 H) at or near δ 3.05 for the CH_2 group and a broad singlet at ~5.7 (1 H) for $CHOCH_3$. Comparison of the chemical shifts of these moieties with those of the methylene groups in VII, X, and XI indicates that the CH_2's in VIIIa and VIIIb are not adjacent to nitrogen and that the methine hydrogens must be α to both the oxygen and nitrogen.

Reactions of isoprene with Ib and Ic were not stereospecific. Approximately equal amounts of the isomeric cycloadducts X and XI were obtained. The major adduct obtained from Ib and isoprene (60% of the total) could be isolated and was assigned structure Xb. The assignment was based primarily on a double-resonance experiment. Decoupling of the C–CH_3 absorption resulted in the appearance of the highest field proton of the C(Ph)CH_2 methylene group as a doublet of doublets ($J_{gem} = 17$, $J_{vic} = 2.7$ Hz)[16] This experiment strongly implies that this methylene and the vinylic methyl group are homoallylic to one another (CH_3-C=CCH_2R) since only second-order coupling (<1 Hz) is expected from the relationship $CH_3(RCH_2)C{=}C{<}$.

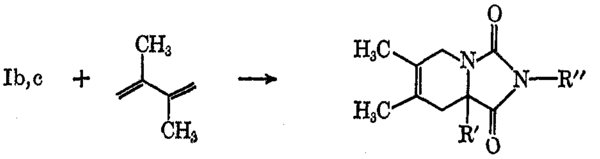


IVa, R′ = H; R″ = CH_3
b, R′ = Ph; R″ = CH_3
c, R′ = CO_2CH_3; R″ = CH_2Ph

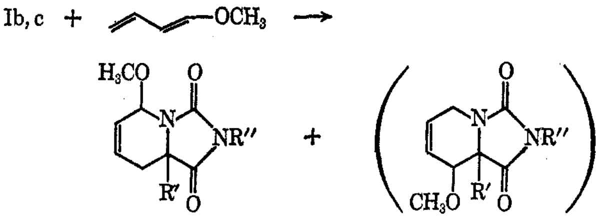


Vb, R′ = Ph; R″ = CH_3
c, R′ = CO_2CH_3; R″ = CH_2Ph

VIb, R′ = Ph; R″ = CH_3

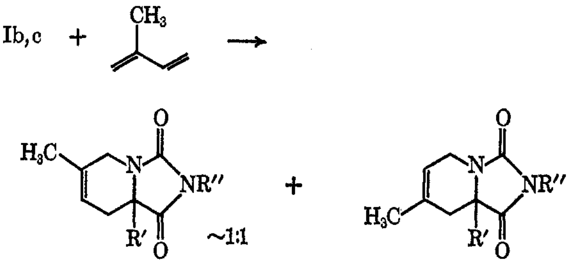


VIIb, R′ = Ph; R″ = CH_3
c, R′ = CO_2CH_3; R″ = CH_2Ph



VIIIb, R′ = Ph; R″ = CH_3
c, R′ = CO_2CH_3; R″ = CH_2Ph

IXb, R′ = Ph; R″ = CH_3
c, R′ = CO_2CH_3; R″ = CH_2Ph



Xb, R′ = Ph; R″ = CH_3
c, R′ = CO_2CH_3; R″ = CH_2Ph

XIb, R′ = Ph; R″ = CH_3
c, R′ = CO_2CH_3; R″ = CH_2Ph

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[13] (a) L. E. Miller and D. J. Mann, *J. Amer. Chem. Soc.*, **73**, 45 (1951); (b) L. E. Miller and C. J. Strickler, *ibid.*, **76**, 698 (1954).

[14] P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964). The size of the coupling is directly related to the dihedral angle between vicinal hydrogens: M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

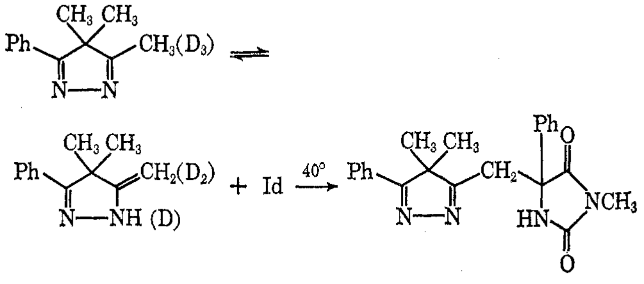
[15] (a) G. I. Poos and M. M. Lehman, *J. Org. Chem.*, **26**, 2575 (1961); (b) K. Alder, F. Brochhagen, C. Kaiser, and W. Roth, *Justus Liebigs Ann. Chem.*, **593**, 1 (1955).

[16] The vicinal coupling $=CH_a—CH_2$– in cyclohexene is 3.1 Hz and in cyclopentene, 2.7 Hz: P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 2017 (1963).

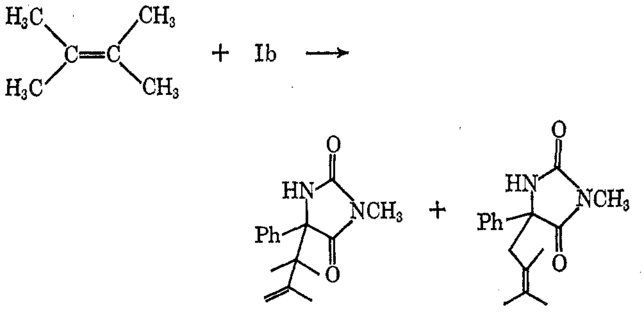
The isomeric adducts Xc and XIc could not be separated nor could the nmr patterns be readily deciphered. Careful examination of the C–OCH$_3$ absorptions, however, revealed two signals of roughly equal intensity which indicated an approximately 1:1 ratio for Xc and XIc.

A number of attempts were made to hydrolyze the cycloadducts IV, V, VIIb, and VIIc, and their dihydro derivatives. Hydrolysis of hydantoins is a general technique for the synthesis of α-amino acids,[17] and in the case of IVb and IVc the amino acids would have been novel ones: 2-aza-3-carboxybicyclo[2.2.1]heptane derivatives. The highly substituted hydantoins IV, V, and VII and their dihydro derivatives proved exceedingly difficult to hydrolyze. They were not attacked by acids or bases under mild conditions, and even under severe conditions, 150–200° in alcoholic KOH, only partially hydrolyzed products were obtained from the hydantoins.

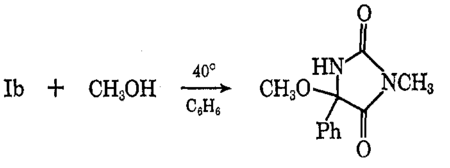
In addition to their dienophilic activity, the dehydrohydantoins also undergo ene-type reactions with cyclohexadiene and 3-phenyl-4,5,5-trimethylisopyrazole to afford VIb and XIIb, respectively. Simple olefins such as tetramethylethylene and cyclohexene did not react at 25°, and cyclohexene did not add even at 80° (40 hr).


XIIb

A photo ene reaction occurred with tetramethylethylene affording the adduct XIIIb; the double-bond isomer XIIIb was apparently present but could not be isolated. In all of these cases, the direction of addition appears to be exclusively that shown, with C–C and N–H bond formation.

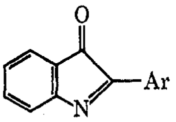

XIIIb XIIIb′

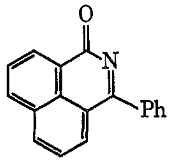
Reaction of the dehydrohydantoins Ia–c with protic reagents is rapid. The order of reactivity is Ia > Ic > Ib. Even with Ib, however, reaction with water or methanol was fast at 40°; addition of methanol to Ib in benzene was followed by nmr spectroscopy and was complete within 30 min at 39°. The dehydrohydantoins do not decompose rapidly in dry air.


XIVc

Discussion

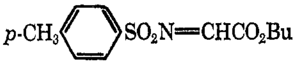
Properties of the Dehydrohydantoins.—The dehydrohydantoins Ia–c are the first reported examples of cyclic α-diacylimines.[5] There have been, however, several studies of cyclic C- or N-monoacylimines; among the compounds studied, only the highly arylated or heteroatom-substituted examples such as XV[18] and XVI[19] were isolable. Less highly substituted derivatives were generally unstable, and only limited circumstantial evidence for their existence was available.[19,20] Several acylic N-acylimines have also been reported,[9,21] but again only specially substituted examples such as XVII[22] and XVIII[23] appear to have significant stability.


XV


XVI

Ph$_2$C=NCOPh

XVII


XVIII

We have observed that the ambient stability of the dehydrohydantoins depends significantly on the substituent on the C=N bond. The 5-phenyl derivative Ib is isolable, thermally stable, and easily handled, although retaining substantial reactivity in polar and cycloaddition reactions. The 5-carbomethoxydehydrohydantoin (Ic) and the unsubstituted compound Ia are progressively less stable. The observed trend in the stability of the dehydrohydantoins is in the direction expected from both steric and electronic considerations; bulky 5 substituents or those capable of conjugation should and do deactivate the imine linkage to attack by nucleophiles.

The extent of interaction of the C=N with the carbonyls in the 2 and 4 positions and with the 5 substituent was assessed by comparison of Ib's ultraviolet spectrum with those of similarly substituted maleimides.

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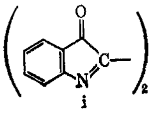
[17] J. P. Greenstein and M. Winitz, Ed., "Chemistry of the Amino Acids," Wiley, New York, N. Y., 1961.

[18] H. S. Ch'ng and M. Hooper, *Tetrahedron Lett.*, 1527 (1969).

[19] A. Warshawsky and D. Ben-Ishai, *J. Heterocycl. Chem.*, **6**, 681 (1969).

[20] Dehydroindigo (i), a well-studied compound, is formally a C-acylimine; however, the imine moiety is part of a 1,4-diazadiene unit.


i

[21] (a) D. Pawellek, *Angew. Chem., Int. Ed. Engl.*, **5**, 845 (1966); (b) W. Lwowski and G. T. Tisue, *J. Amer. Chem. Soc.*, **87**, 4022 (1965); (c) Yu. Z. Zeifman, N. P. Gambaryan, and I. L. Knunyants, *Izv. Akad. Nauk. SSSR*, 2046 (1965).

[22] G. Reddelien and H. Danilof, *Chem. Ber.*, **54**, 3132 (1921).

[23] R. Albrecht and G. Kresze, *ibid.*, **98**, 1431 (1965).

TABLE I

ULTRAVIOLET AND INFRARED ABSORPTIONS OF Ib AND ITS ANALOGS

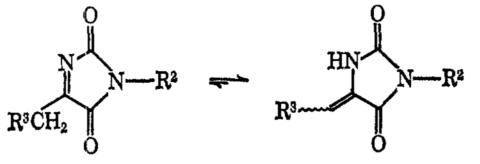
Compd	Infrared absorption $\gamma_{C=N}$ or $_{C=C}$, cm^{-1}	Infrared absorption Solvent	Ultraviolet absorption (max) nm (ϵ)	Ultraviolet absorption (max) Solvent
Ib	1590, 1563	$CHCl_3$	284 (9600) 325 (4925)	CH_3CN
3-Phenyl-2-azanaphthoquinone[a]	1660, 1572	Nujol	316 (10,200) 500 (200)	CH_2Cl_2
3-Phenyl-1-isopropylmaleimide			223 (12,400)[b] 270 (9400) 342 (3500)	95% EtOH
3-Phenylmaleic anhydride			216 (9600)[b] 240 (3200) 312 (10,200)	Isooctane
1-Isopropylmaleimide			217 (12,300)[b] 223 (10,800) 301 (520)	Isooctane
5-Benzylidenehydantoin[c]			255 (3400) 320 (23,400)	
XVI	1640[d]	$CHCl_3$		
XVIII	1625[e]			
2-Phenylpyrazoline-1	1615[f]	Film		

[a] Reference 5b. [b] C. S. Rondestvedt, Jr., M. J. Kalm, and O. Vogl, *J. Amer. Chem. Soc.*, **78**, 6115 (1956). [c] Reference 7. [d] Reference 19. [e] Reference 23. [f] M. C. Kloetzel, J. L. Pinkus, and R. M. Washburn, *J. Amer. Chem. Soc.*, **79**, 4222 (1957).

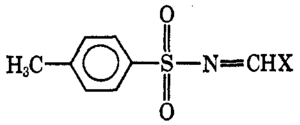
The data in Table I indicate that Ib is a cross-conjugated system identical with its olefinic analogs. Both Ia and Ic appear to be colorless, as are their olefinic analogs.

Infrared spectroscopy provides further evidence of conjugation between the imine carbonyls and the 5 substituent. The intense doublet at 1590 and 1563 cm^{-1} can be assigned to the C=N stretch by virtue of its position and the absence of such absorptions in the spectra of IIb–XIIIb. Both the unusually low frequency and the high intensity of these bands are indicative of resonance interactions.

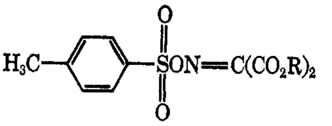
It is of interest at this point to comment on the position of the equilibrium between 5-alkyldehydrohydantoins and the 5-methylene (enamide) tautomers.[5] The isolation of the 5-methylene isomers exclusively under what must have been equilibrating conditions indicate that the equilibrium lies very far to the right.[5,6,8] Our results, which indicate that 5-alkyldehydrohydantoins should have limited atomospheric stability, support this since reaction of the 5-alkyldehydrohydantoin tautomer would lead to rapid deterioration of the samples. In most monounsaturated five-membered rings, the isomer with the double bond exocyclic to the ring has substantial stability;[24] however, in the hydantoin series the equilibrium lies far in this direction. The most important factors in driving this equilibrium toward the enamide are probably the energy gained by delocalization of the nonbonding electrons on the 1-N into the adjacent carbonyl and the formation of an N-H bond; this and the delocalization energy of the α,β-unsaturated amide must be large enough to counterbalance any benefit due to delocalization of the π electrons in the cross conjugated dehydrohydantoin.



Cycloaddition Reactions.—There are two reports in the literature of acylic imines with dienophilic reactivity. Kresze and Albrecht observed in 1964[23,25] that N-trichloro-, N-trifluoro- and N-carbobutyloxylethylidene *p*-toluenesulfonamides



where X = CCl_3, CF_3, or CO_2Bu, underwent the Diels–Alder reaction with various dienes at 80°. From their data one can estimate that these are active dienophiles. Sometime after our researches in the area had begun, Biehler, *et al.*,[26] reported that certain derivatives of isonitrosomalonic esters, *e.g.*



reacted with cyclopentadiene at 25°. This work unfortunately does not give a good indication of dienophilic activity since cyclopentadiene is the most reactive simple diene by several orders of magnitude.[3] The study is of considerable interest, however, since the cycloadducts should be readily hydrolyzable to amino acids.

Very recently Goldstein and Ben-Ishai[6a] communicated that reaction of various 3-substituted 5-methoxyhydantoins at 80° with acids in the presence of dienes affords satisfactory yields of Diels–Alder adduct. In certain cases products of carbonium ion reactions between the hydantoin and diene were also observed. Their results can be interpreted, in the light of our data, as due to the reversible formation of the 3-substituted dehydrohydantoins by way of the 5-carbonium ions.

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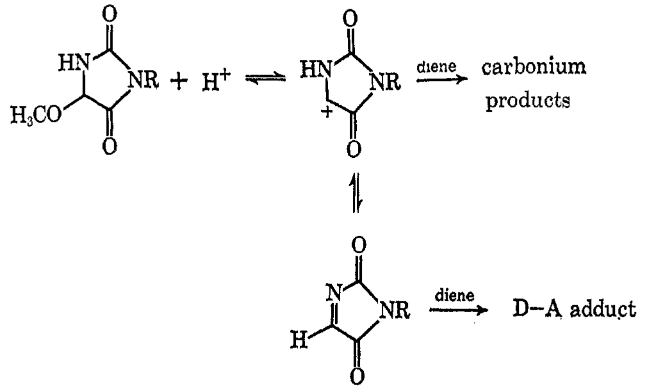
(24) Itaconic anhydride is stable at ambient temperatures but under equilibrating conditions is converted to citraconic anhydride: R. L. Shriner, S. G. Ford, and L. J. Roll, "Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1943, p 368; W. G. Barb, *J. Chem. Soc.*, 1647 (1955).

(25) G. Kresze and R. Albrecht, *Chem. Ber.*, **97**, 490 (1964).

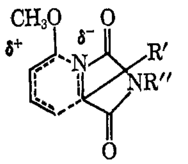
(26) J.-M. Biehler, J.-P. Fleury, J. Perchais, and A. Regent, *Tetrahedron Lett.*, 4227 (1968).

Reaction of the dehydrohydantoins or the ions with dienes are slower than reaction with methanol but are irreversible. This system is useful for the preparation of certain cycloadducts of dehydrohydantoins. Its limitations result from the presence of methanol and acid which preclude observation or isolation of the dehydrohydantoin and the utilization of most heteroatom-substituted dienes.



The dehydrohydantoins Ia–c are reactive dienophiles, surpassing the previously reported acyclic imines and the cyclic monoacylimines in their activity. This appears to be true even for Ib in which the phenyl group affords a substantial steric hindrance to cycloaddition. The increase in activity obtained by incorporation of the imine moiety into a five-membered ring is consistent with results obtained with olefins and azo systems.[2] Attempts to compare the activity of comparably substituted C=C, C=N, N=N dienophiles are not wholly successful owing to the difficulty of evaluating the parent dehydrohydantoin system, Ia. The 5-phenyl-3-methyldehydrohydantoin appears to be more reactive with isoprene than 3-phenylmaleic anhydride by a factor of 5–10 and less reactive than N-phenylmaleimide by a similar amount. The 5-carbomethoxy-3-benzylhydantoin is substantially more reactive with isoprene and 1-methoxybutadiene than is maleic anhydride or N-phenylmaleimide and appears to be comparable in reactivity to an extremely active diene such as tricyanoethylene.[27] The high reactivity of Ic is, in part, accounted for by the presence of three electron-withdrawing substituents. Observations made by Sauer and coworkers[2] indicate that a 1,1,2 arrangement of cyano groups on an olefin is much more strongly activating ($>10^3$ times) for Diels–Alder addition than is a 1,2 arrangement. Quantitative data on triacyl olefins are not available for comparison with Ic; however, Russian work indicates that ethylidenemalonate is more reactive than maleic anhydride.[28] Unfortunately, data on Ib and Ic cannot be extrapolated with much confidence to the case of Ia, although our feeling is that Ia's activity is intermediate between that of N-phenylmaleimide and 4-phenyl-1,2,4-triazoline-3,5-dione, but closer to the former.

Reaction of 1-methoxybutadiene with either Ib or Ic affords only the cycloadduct with the methoxyl group α to nitrogen and probably *trans* to the phenyl or carbomethoxyl substituent. The observed regioselectivity has an analogy in the reports that 1-substituted butadienes (both electron-donating and -withdrawing substituents) react with monoacyl ethylenes to form primarily the 1,2-disubstituted cyclohex-3-enes.[29] The explanation for the orientational selectivity in the carbocyclic systems is not known. In our reactions the preference is consistent with the contribution of polar structures to the transition state since charge delocalization is most favorable for XIXc. Other evidence (*vide infra*) indicates that the transition and ground states have similar polarities; however, the reactants used in these studies have dipoles and so a transition structure with some small amount of polar character is possible. The stereochemical relationship of the methoxyl and R′ groups cannot be rigorously deduced from the nmr spectrum; however, a *trans relationship* is predicted by the Woodward–Hoffmann rules[30] and is expected from the earlier empirical correlations of Alder.[29a]



XIXb, R′ = Ph; R″ = CH_3
c, R′ = CO_2CH_3; R″ = CH_2Ph

Reactions of isoprene with either Ib or Ic show little selectivity and afford roughly equal amounts of the two positional isomers. In contrast, the reaction of isoprene with either 3-phenyl- or 3-*p*-nitrophenylmaleic anhydride[13] or with N-carbobutyloxyethylidene-*p*-toluenesulfonamide[25] is highly stereospecific affording the isomer with methyl and aryl groups in a *para* relationship. Consideration of the various alignments of isoprene with Ib, Ic, and the dienophiles cited above does not reveal a single transition state that is as highly favored by electronic considerations as is XIX.

A perturbational MO method has recently been applied with some success to the prediction of isomer mixtures from the reaction of unsymmetrical dienes and dienophiles.[31] However, the technique was utilized for substantially simpler systems. The complexity of the dienophiles considered here makes the contradictions between our results and those of Miller[13] and of Kresze[23,25] unexceptional.

The rates of reaction of Ib and 1-methoxybutadiene in solvents with very different dielectric constants (CD_3CN and C_6D_6–$CDCl_3$) were essentially the same. A more detailed investigation of solvent effects was not made because of the anticipation of severe problems due to reaction of Ib with the solvents. The indication is, however, that there is little charge separation in the transition state.

The characteristic features of the reaction between dehydrohydantoins and dienes are the regiospecificity of product formation (in nearly all cases), the apparent absence of solvent effects, and the rate enhancement caused by electron-donating groups on the diene.

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(27) Reaction rate of tricyanoethylene with cyclopentadiene is fast: $k = 4.8\ \text{l. mol}^{-1}\ \text{sec}^{-1}$.[2b]

(28) B. A. Arbusov and E. G. Kataev, *Zh. Org. Khim.*, **20**, 68 (1950).

(29) (a) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937); (b) M. G. Ettlinger and E. S. Lewis, *Tex. J. Sci.*, **14**, 58 (1962); (c) J. C. Martin and R. K. Hall, *Chem. Rev.*, **61**, 537 (1961).

(30) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4388 (1965); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

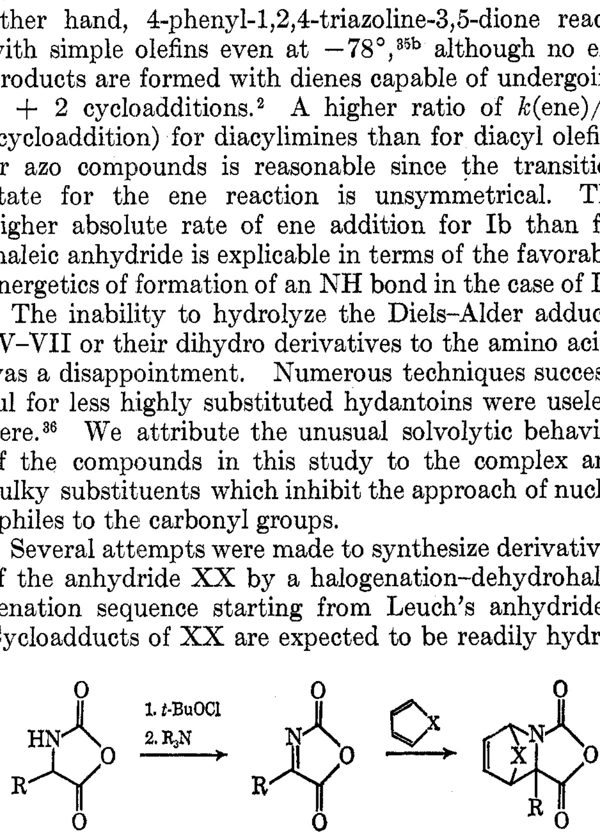
(31) J. Feuer, W. C. Herndon, and L. H. Hall, *Tetrahedron*, **24**, 2575 (1968).

These same phenomena are prominent in the concerted 4 + 2 cycloaddition[30] of olefins to dienes, and the two reactions appear to have the same mechanism.[32]

The ene-type additions of Ib with cyclohexadiene, 3-phenyl-4,4,5-trimethylisopyrazole, and tetramethylethylene (photochemically) are among the first examples of this reaction with imines.[33] The activity of α-diacylimines in the ene reaction appears to be intermediate between that of the olefinic[34] and azo analogs.[35] Neither cyclohexadiene nor 3-phenyl-4,5,5-trimethylisopyrazole form ene adducts with maleic anhydride under conditions close to those at which Ib reacts. On the other hand, 4-phenyl-1,2,4-triazoline-3,5-dione reacts with simple olefins even at −78°,[35b] although no ene products are formed with dienes capable of undergoing 4 + 2 cycloadditions.[2] A higher ratio of k(ene)/k(cycloaddition) for diacylimines than for diacyl olefins or azo compounds is reasonable since the transition state for the ene reaction is unsymmetrical. The higher absolute rate of ene addition for Ib than for maleic anhydride is explicable in terms of the favorable energetics of formation of an NH bond in the case of Ib.

The inability to hydrolyze the Diels–Alder adducts IV–VII or their dihydro derivatives to the amino acids was a disappointment. Numerous techniques successful for less highly substituted hydantoins were useless here.[36] We attribute the unusual solvolytic behavior of the compounds in this study to the complex and bulky substituents which inhibit the approach of nucleophiles to the carbonyl groups.

Several attempts were made to synthesize derivatives of the anhydride XX by a halogenation–dehydrohalogenation sequence starting from Leuch's anhydrides. Cycloadducts of XX are expected to be readily hydrolyzable. However, all attempts to prepare XX were unsuccessful. The recent work of Biehler, *et al.*, provides an amine dienophile that is more convenient for cases where the amino acid derivable from the cycloadduct is of interest.



XX

The addition of nucleophiles to simple imines are facile reactions,[37] and, as expected, the presence of electron-withdrawing groups accelerates the rate of such additions substantially. There have been several studies of the reaction of nucleophiles with acyl- and sulfonylimines.[19,21c,23,38] We have, accordingly, not studied the addition of nucleophiles to dehydrohydantoins in detail. The mild conditions under which methanol adds to even Ib and the atmospheric instability of Ia and Ic indicates the ease with which such reactions occur. The reactivity of Ia–c should be similar to that of N-acylimines since attack of nucleophiles occurs on the carbon end of the imine bond affording the stabilized amide anion. The reactivities of Ib, 3-phenyl-2-azanapthoquinone,[5b] and XVI[19] toward methanol appear to be comparable.

Experimental Section

All experiments were carried out in a moisture-free, nitrogen atmosphere, unless otherwise indicated. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., or ERA, Brussels, Belgium. Mass spectra were obtained by I. R. Ladd, Union Carbide Research Institute, Tarrytown, N. Y. Nmr studies at 220 Hz and decoupling studies at 60 Hz were carried out by Dr. E. B. Whipple and M. Ruta of the Union Carbide Research Institute.

Hydantoins IIa, b.—3-Methylhydantoin (IIa) was prepared by reaction of methyl isocyanate and glycine ethyl ester to form the ethyl ester of methylhydantoic acid, followed by cyclization in hot hydrochloric acid.[39] Yields based on the glycine ethyl ester were 40–50%. Methylation of hydantoin (Eastman) with methyl sulfate in aqueous sodium hydroxide[40] afforded IIa in 20–30% yield.

Reaction of 5-phenylhydantoin (K and K) with methyl sulfate in aqueous base afforded 5-phenyl-3-methylhydantoin (IIb) in 50–65% yields.

3-Benzyl-5-carbomethoxyhydantoin (IIc).—A solution of 100 g of hydantoin in 500 ml of 2 *M* NaOH was treated in a dropwise fashion with 220 ml of benzyl chloride. The reaction mixture was then heated at reflux for 20 hr. Cooling and pouring onto ice afforded 40 g of crystalline material. Drying and recrystallization from benzene gave 35 g of 3-benzylhydantoin.

Addition of 9.5 g of the 3-benzylhydantoin to 50 ml of a 2 *M* solution of $MgCO_3$ in dimethylformamide saturated with CO_2[41] and heated for 3 hr at 80° afforded a gelatinous, crystalline precipitate. This was poured into 250 ml of dry ether, the ether was decanted from the crystals, and 200 ml of cold methanol (−78°) saturated with HCl was added. The reaction mixture was then stirred overnight. Filtration yielded 4.3 g of colorless crystals, mp 137–141°. Recrystallization from benzene gave 3.7 g (38%) of 3-benzyl-5-carbomethoxyhydantoin as colorless crystals, mp 140–142° (lit.[41a] mp 134–136°).

Attempts to prepare 3-benzyl-5-acetylhydantoin by a similar technique[41a] were unsuccessful.

1-Chlorohydantoins IIIa–d.—Compounds IIa–c were chlorinated in an identical manner except that acetonitrile was utilized as the solvent with IIc. The reactions were run in the atmosphere. A solution of 1.00 g (5.3 mmol) of IIb was slurried in 25 ml of methanol and 0.6 g of *t*-BuOCl (K and K) diluted to 5 ml with benzene added dropwise. Removal of a sample of the reaction mixture after 2 hr and examination by infrared spectroscopy ($CHCl_3$) indicated the absence of N–H bonds (no absorption at 3450 and 3250 cm^{-1}). The nmr spectra ($CDCl_3$) contained a singlet at δ 5.3 (CH–N) establishing that chlorination had occurred at the 1 position (on N). Removal of the volatiles on a rotary evaporator afforded IIIb as colorless crystals, mp 122–124°, which were dried *in vacuo* [50° (0.02 mm)] prior to use.

Reaction of Ia and Cyclopentadiene.—A solution of 0.5 g (4.3 mmol) of IIIa in 10 ml of benzene was added dropwise to a solution of 6 ml of cyclopentadiene (freshly cracked), 0.5 ml of triethylamine, and a few milligrams of hydroquinone in 10 ml of benzene at 25°. The solution remained clear throughout most of the addition, but after a further 2 hr it turned yellow and a precipitate formed. Removal of the solvent *in vacuo* and ex-

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[32] For recent discussions of the mechanism of the Diels–Alder reaction, see ref 2 and 30, and also A. Wasserman, "Diels–Alder Reactions," Elsevier, Amsterdam, 1965.

[33] After the completion of this manuscript, a report appeared of the reaction of 3-benzyl-5-methoxyhydantoin with olefins at 80° in the presence of acids. The results suggest that the 5-carbonium ion and the dehydrohydantoin have both been generated and have reacted with the olefin present. Some of the additions are probably by an ene mechanism: D. Ben-Ishai and G. Ben-Et, *Chem. Commun.*, 1399 (1969).

[34] K. Alder and M. Schumacher, "Fortschritte der Chemie Organishen," Part I, W. Forest, Ed., Verlag Chemie, Berlin, 1943, p 251.

[35] (a) B. T. Gillis and P. E. Beck, *J. Org. Chem.*, **27**, 1947 (1962); (b) W. H. Pirkle and J. C. Stickler, *Chem. Commun.*, 760 (1967).

[36] Hydantoins are easily hydrolyzed when lightly substituted; however, highly substituted systems resist hydrolysis: H. Aspelund and P. Waselius, *Acta Acad. Abo., Math. Phys.*, **27**, 18 (1967); *Chem. Abstr.*, **68**, 49512M (1968); M. Lora-Tamayo, R. Madronero, and C. Ochoa, *An. Quim.*, **64**, 591 (1968); *Chem. Abstr.*, **69**, 106154 (1968).

[37] R. W. Layer, *Chem. Rev.*, **63**, 489 (1963).

[38] R. Albrecht, G. Kresze, and B. Mlakar, *Chem. Ber.*, **97**, 483 (1964).

[39] J. R. Bailey, *J. Amer. Chem. Soc.*, **26**, 1006 (1904).

[40] A. Kjaer, *Acta Chem. Scand.*, **4**, 893 (1950).

[41] (a) H. Finkbeiner, *J. Org. Chem.*, **30**, 3414 (1965); (b) French Patent 1,389,841 (Feb 19, 1965); *Chem. Abstr.*, **62**, 16258 (1965).

amination of the residue by nmr ($CDCl_3$) revealed two singlets in in the $N-CH_3$ region, at δ 3.03 and 2.91. Chromatography of the residue on Florisil using benzene–chloroform as the eluent afforded 0.075 g of colorless oil, which was homogeneous by tlc (silica gel; $CHCl_3-CH_3OH$). Attempts to crystallize the oil were unsuccessful. The nmr spectrum ($CDCl_3$) of the material had absorption at 1.88 (m, CH_2), 2.90 (s, NCH_3), 3.58 (m, $=C-CH$), 4.28 (d, J = 3.1 Hz, NCHCO), 4.75 (m, =CCHN), 6.34 (m, $CH=CH$). The infrared spectrum ($CHCl_3$) had bands at 1780 and 1710 cm^{-1}. The spectral data are in agreement with the structure IVa: 4-methyl-2,4-diazatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione.

The yield was not improved by variation in the reaction conditions. Reaction with other dienes were unsuccessful.

5-Phenyl-3-methyldehydrohydantoin (Ib).—A well-stirred suspension of 1.15 g (5.3 mmol) of 1-chloro-5-phenyl-3-methylhydrohydantoin (IIIb) in 25 ml of benzene (dried over sodium wire) was treated in a dropwise fashion with a solution of 0.59 g (5.1 mmol) of tetramethylethylenediamine in benzene. A yellow color was observed after the first drop and became increasingly more intense. After the completion of addition, the reaction mixture was stirred for an additional 30 min and the yellow solution decanted into a second flask *via* a Tygon tube fitted with a glass wool plug. The solution of Ib was either utilized directly or was worked up. Isolation of Ib was accomplished by removal of the volatiles *in vacuo* [25° (0.02 mm)], insertion of a cold finger into the flask, and sublimation [60° (0.02 mm)]. The isolated yield of yellow, crystalline Ib, mp 148–150°, was 0.65 g (66%). The melting point was not changed by repeated sublimation. The product could be handled and even stored for several days in the atmosphere.

Reaction of Ib with Cyclopentadiene.—A slurry of IIIb (prepared from 51.5 mmol of IIb) in 50 ml of benzene was added dropwise to a solution of 3.24 ml of tetramethylethylenediamine, 20 ml of freshly distilled cyclopentadiene, and a trace of hydroquinone in benzene. The solution became yellow-brown and was stirred overnight. After removal of the volatiles the reaction mixture was worked up by column chromatography (Florisil, hexane–chloroform) and afforded 9.1 g (68%) of crystalline material, mp 115–118°. Recrystallization from ether–hexane afforded 8.8 g of colorless crystals, mp 118–119°, which were identified as 6-phenyl-4-methyl-2,4-diazatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (IVb).

Hydrogenation of IVb in EtOAc over Adams catalyst (1 atm of H_2) afforded the dihydro derivative of IVb, 6-phenyl-4-methyl-2,4-diazatricyclo[5.2.1.$0^{2,6}$]deca-3,5-dione, in quantitative yield, mp 157–158°.

Reaction of Ib with Cyclohexadiene.—A solution of 0.100 g (0.53 mmol) of Ib and 1 ml of cyclohexadiene was stirred at 40° for 10 hr. Removal of the solvent *in vacuo* and examination of the residue by nmr spectroscopy ($CDCl_3$) indicated the presence of two products (two N-methyls, at δ 2.88 and 3.0) in the ratio of 4.5:1. The minor product, mp 216–218°, was isolated by column chromatography and recrystallized from $CHCl_3$; it was identified (see Table II) as 5-(cyclohexa-2,5-dienyl)-5-phenyl-3-methylhydantoin (VIb). The major product crystallized from hexane–chloroform, mp 210–211°, and was identified as the cycloadduct, 6-phenyl-4-methyl-2,4-diazatricyclo[5.2.2.$0^{2,6}$]undec-8-ene-3,5-dione (Vb).

Reaction of Ib and 2,3-Dimethylbutadiene.—The reaction was carried out as described for cyclopentadiene except that the starting material was 25.6 mmol of IIb and the reaction mixture was heated overnight at 60°. The yield of crude 6-phenyl-3,4,8-trimethyl-1,8-diazabicyclo[4.3.0]non-3-ene-7,9-dione (VIIb) was 4.34 g (60%). Recrystallization from ether–hexane afforded 3.8 g of colorless crystals, mp 159.5–162°.

1-Methoxybutadiene and Ib.—To a solution of 5.0 ml of 1-methoxybutadiene and a few milligrams of hydroquinone in 10 ml of dry benzene at 25° was added 0.450 g (2.4 mmol) of sublimed Ib. The yellow color of the solution faded rapidly and a precipitate formed. The reaction was complete within 90 min. The initial precipitate was 0.280 g of crystalline material, mp 147–150°. Removal of the volatiles on a rotary evaporator left a yellow oil. Trituration with ether–pentane afforded an additional 0.305 g. The combined precipitate, 0.585 g (86%), showed a single spot in tlc (silica gel; benzene–2-propanol, 9:1). Recrystallization afforded colorless crystals, mp 157–159.5°. The infrared ($CHCl_3$) had bands at 1775, and 1715 and 1070 cm^{-1}, among others. The nmr spectrum ($CDCl_3$) had absorptions at δ 3.02 (s, NCH_3), 3.51 (s, OCH_3), 5.72 (m, $CHOCH_3$), 5.75–6.1 (m, 2 CH=), and 7.43 (m, 5) as well as an AB pattern centered at δ 3.0. The 220-MHz spectrum resolved the AB pattern and permitted determination of the couplings; the geminal coupling is 16 Hz and the low-field AB proton is coupled, J_{vic} = 7 Hz, to the low-field vinylic hydrogen while the high-field AB proton and the $CHOCH_3$ show only small coupling (1–2.5 Hz) with the vinylic hydrogens.

Anal. Calcd for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.95; N, 10.29; O, 17.83. Found: C, 66.32; H, 5.86; N, 10.17.

A solution of 0.063 g (0.33 mmol) of Ib and 0.020 g (0.24 mmol) of 1-methoxybutadiene in 0.50 ml of benzene-d_6 and $CDCl_3$ (1:1) was placed in the probe of the A-60 mass spectrometer (39°), and the disappearance of Ib and the formation of VIIIb were followed by repeated integration of the OCH_3 and NCH_3 absorptions. After 35 min, 50% of Ib had reacted. The rate of disappearance of 0.064 g of Ib in the presence of 0.020 g of 1-methoxybutadiene in 0.5 ml of CD_3CN was followed similarly; 50% of Ib had reacted at the end of 30 min. In neither case were products other than VIIIb formed in observable concentrations.

Isoprene and Ib.—A solution of 0.100 g (0.53 mmol) of Ib and 2 ml of isoprene in 10 ml of dry benzene was heated at 40° for 12 hr. The yellow color of the solution gradually faded and a fine white precipitate (polymer) formed. After removal of the volatiles, the crude reaction mixture was examined by nmr spectroscopy. The spectrum ($CDCl_3$) contained, among other signals, absorptions at δ 1.66 and 1.47 ($=CCH_3$) with an area ratio of 3:2. The reaction mixture was chromatographed on Florisil and a homogeneous, crystalline fraction, 0.102 g (75%), obtained. Crystallization from chloroform–hexane resulted in the selective precipitation of the major isomer, mp 131–133°. The infrared spectrum had bands at 1770 and 1710 cm^{-1}. The nmr spectrum ($CDCl_3$) had absorptions at δ 1.73 (m, $=CCH_3$), 3.07 (s, NCH_3), 5.42 (m, 1), and 7.42 (m, 5) in addition to AB patterns centered at δ 2.77 and 4.12. The protons of the high-field AB pattern absorb at δ 2.54 and 2.95 with J_{gem} = 16 Hz while in the low-field pattern the protons absorb at δ 4.54 and 3.62 and J_{gem} = 19 Hz. Decoupling of the C-methyl group led to sharpening of the proton at δ 2.54 into a doublet, J = 2.7 Hz, due to coupling with the vinylic hydrogen. The major isomer is accordingly assigned structure Xb, 5-phenyl-3,7-dimethyl-1,8-diazabicyclo-[4.3.0]non-3-ene-7,9-dione. Subsequent crystalline fractions contained a mixture of both isomers.

Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.11; H, 6.21; N, 10.89.

Competition between Ib and N-Phenylmaleimide for 2,3-Dimethylbutadiene.—A solution of 0.100 g (0.53 mmol) of Ib, 0.0935 g (0.54 mmol) of N-phenylmaleimide, and 45 μl (0.40 mmol) of 2,3-dimethylbutadiene was stirred for 16 hr at 25°. Removal of the solvent *in vacuo* and examination of the residue by nmr spectroscopy ($CDCl_3$) revealed absorptions at δ 1.73 (s, CH_3) and 2.48 (m, CH_2) due to 8-phenyl-3,4-dimethyl-8-azabicyclo[4.3.0]non-3-ene-7,9-dione and minor absorptions at δ 1.58 and 3.07 assignable to VIIb. Resonances due to the starting materials were present at δ 3.07 (s, NCH_3) and 6.88 (s, CH=CH). Comparison of the integrals indicates that the ratio of VIIb to the adduct of N-phenylmaleimide and 2,3-dimethylbutadiene is no more than 1:10 and possibly less.

Reaction of Ic and Cyclopentadiene.—A solution of IIIc (prepared from 1.0 g of IIc) in 20 ml of dry benzene was added dropwise at 25° to a solution of 10 ml of cyclopentadiene (freshly distilled), 0.65 ml of triethylamine, and a trace of hydroquinone. The solution became yellow and then tan and a precipitate formed. After 2 hr, the volatiles were removed and the oily residue purified by column filtration (Florisil; hexane–$CHCl_3$ eluent). The crude yield of cycloadduct (homogeneous by tlc on silica gel with chloroform–methanol, 9:1) was 0.98 g (79%). Crystallization from hexane afforded 0.85 g (69%) of colorless crystals, mp 111.5–113.5°, which were identified as 6-carbomethoxy-4-benzyl-2,4-diazatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (IVc) (see Table II).

Reaction of Ic with Cyclohexadiene.—The reaction was carried out exactly as described above except that the reaction mixture was stirred overnight prior to work-up. The crude yield of cycloadduct, mp 107–111°, was 0.580 (60%). Recrystallized material (ether–hexane) had mp 110–111° and was shown to be 6-carbomethoxy-4-benzyl-2,4-diazatricyclo[5.2.1.$0^{2,6}$]undec-8-ene-3,5-dione (Vc) (see Table II).

Reaction of Ic with Isoprene.—The reaction was carried out and worked up as above except that 0.320 g (1.15 mmol) of

TABLE II

Compd	Mp, C°	Ir,[a] cm^{-1}	Nmr,[b] δ
IIb	163	3460, 3250 1780, 1720	3.05 (s, 3)[c] 5.28 (m, 1); 7.53 (m, 5)
IIIb	123–125[d]	1795, 1730	
Ib	148–150[e]	1800, 1730 1590, 1563	3.18 (s, 3) 7.3–7.8 (m, 5)
IVb[f]	118–119[g]	1775, 1710	1.25–1.9 (m, 2) (s, 3) 3.63 (m, CHC=), 4.85 (m, NCHC=) 5.92 (m, CH=) 6.52 (m, CH=) 7.27–7.9 (m, 5)
6-Phenyl-4-methyl-2,4-diazatricyclo[5.2.1.0^{2,6}]deca-3,5-dione[g]	156–158	1775, 1715	1.2–2.2 (7); 3.00 (s, 3) 4.36 (m, 1) 7.3–7.85 (m, 5)
Vb[g]	210–211[h]	1780, 1720	1.1–2.1 (m, 4) 2.85 (s, NCH$_3$) 3.52 (m, CHC=) 4.98 (m, NCH=) 6.5 (m, 2CH=) 7.3–7.9 (m, 5)
6-Phenyl-4-methyl-2,4-diazatricyclo[5.2.2.0^{2,6}]undeca-3,5-dione[f]	134–135	1780, 1715	1.1–2.3 (m, 8); 2.78 (m, 1) 4.25 (m, CHN) 2.97 (s, NCH$_3$) 7.3–7.9 (m, 5)
VIb[f]	216–218[i]	3460, 3300 1775, 1700[j]	2.7 (m, 2) 3.02 (s, NCH$_3$) 3.8 (m, 1) 5.1–6.1 (m, 4) 7.3–7.9 (m, 5)
VIIb[f]	159.5–162.5[k]	1770, 1710	1.58 (s, 3); 1.7 (s, 3) 2.5–2.9 (m, 2) 3.08 (s, 3) 3.25–3.8 (m, 2) 7.42 (3, Ph)
XIIb[f]	208.5–210[l]	3400, 1785 1715	1.05 (s, 3) 1.38 (s, 3) 3.08 (s, NCH$_3$) 3.10 (d, 1; J = 17 Hz) 3.62 (d, 1; J = 17 Hz) 7.2–8.2 (m, 11)
XIIb-d_3			1.05 (s, 3); 1.38 (s, 3) 3.08 (s, NCH$_3$) 7.2–8.2 (10)
XIIIb	206–208[m]	3440, 3240 1770, 1708	1.27 (s, 6) 1.47 (s, 3); 3.01 (s, 3) 5.04 (m, 2) 7.25–7.9 (m, 5)
XIVb[f]	134.5–136[d]	3440, 3250 1790, 1730	3.08 (s, NCH$_3$) 3.52 (s, OCH$_3$) 6.6 (m, NH) 7.35–7.9 (m, 5)
IIIc[f]	142–143	3460, 3250 1780, 1720	3.82 (s, 3)[c] 4.67 (m, CHN, NCH$_2$Ph) 6.7 (m, NH); 7.34 (m, 5)
IVc[f]	111.5–113.5[l]	1790, 1750 1720	1.88 (m, 2) 3.76 (s, 3) 3.9 (m, CH—C=) 4.57 (s, CH$_2$N) 4.76 (m, NCHC=) 6.35 (m, 2)
Vc[f]	110–111[n]	1790, 1745	1.3–2.1 (m, 4) 3.58 (m, CH—C=) 3.8 (s, OCH$_3$); 4.61 (s, CH$_2$N) 4.82 (N—CH=C) 6.37 (m, 2)

[a] In CHCl$_3$ unless otherwise indicated. [b] In CDCl$_3$ unless otherwise indicated. [c] In (CD$_3$)$_2$CO. [d] Yield 95–100%. [e] Yield 60–70%; mass spectral analysis (70 eV): 188 (36; pp); 131 (17), 103 (100), 77 (6), 76 (14). [g] Yield 70%. [f] Satisfactory combustion analyses (±0.4%) have been obtained for these compounds (Ed.). [h] Yield 53%. [i] Yield, 10%. [j] KBr pellet. [k] Yield 50%. [l] Yield 80%. [m] Yield 20%. *Anal.* Calcd: C, 70.55; H, 7.40. Found: C, 69.95; H, 7.13. [n] Yield 60%.

IIIc, 0.20 ml of tetramethylethylenediamine, and 5 ml of isoprene were employed. The reaction required less than 1 hr at 25°. The cycloaddition products Xc and XIc were obtained after chromatography in a combined yield of 0.167 g (55%). The mixture was a colorless oil which was homogeneous by tlc (silica gel, benzene–2-propanol, 9:1). It could not be crystallized or sublimed.

The nmr spectrum ($CDCl_3$) of the mixture was extremely complex; there were absorptions at δ 1.67 (m, C–CH_3), 3.79 and 3.80 (s, OCH_3), 4.73 (s, CH_2Ph), and 5.49 (m, =CH), in addition to ill-defined multiplets (AB patterns by analogy to Xb and XIb) centered at δ 2.67 and 4.0. The observation of two CO_2CH_3 absorptions of roughly equal intensity at δ 3.80 indicates that the two isomers are present in approximately equal amounts. The infrared spectrum ($CHCl_3$) had absorptions at 1790, 1750, and 1725 cm^{-1}, among others. The mass spectrum (70 eV) had *m/e* 314 (23; pp), 256 (15), 255 (38), 91 (100), and 66 (14) as major fragments.

Reaction of Ic with 1-Methoxybutadiene.—The cycloaddition was carried out as described for isoprene. The reaction was over within 10 min of the completion of addition of IIIc. The yield of chromatographed material (homogeneous by tlc) was 72%, mp 115–118°. The nmr spectrum ($CDCl_3$) of the crude chromatographic residue indicated that a single product was formed; the spectrum ($CDCl_3$) had absorptions at δ 3.41 (s, OCH_3), 3.84 (s, CO_2CH_3), 4.73 (s, NCH_2Ph), 5.67 (m, $CHOCH_3$), 5.83 (m, 1, =CH), and 7.40 (m, 5) as well as an AB pattern whose two protons absorb at δ 2.51 and 3.26. The AB protons are coupled to each other by 16 Hz and the proton at δ 3.26 is split by the lowest field vinylic hydrogen, J = 6 Hz. Recrystallization from methylene chloride–hexane afforded colorless crystals, mp 117–118.5°, identified as 6-carbomethoxy-2-methoxy-4-benzyl-2,4-diazabicyclo[4.3.0]non-3-ene-7,9-dione (VIIIc).

Anal. Calcd for $C_{17}H_{18}N_2O_5$: C, 61.81; H, 5.49; N, 8.48. Found: C, 61.22; H, 5.47; N, 8.22.

Attempted Hydrolysis of IV, V, VI, and Their Hydrolysis Derivatives.—Various conditions were utilized in an attempt to hydrolyze the Diels–Alder adducts and their dihydro derivatives. The experiments described here are representative. A solution of 1.0 g (3.7 mmol) of Vb and 1.2 g (2.1 mmol) of potassium hydroxide in 20 ml of ethylene glycol was heated under reflux for 70 hr. Removal of the alcohol *in vacuo*, addition of water, and extraction with ether afforded, after removal of the ether solvent, 0.75 g of Vb. Analysis of the residue by tlc (silica gel–10% methanol in chloroform) indicated that several products had been formed but in amounts too small to isolate.

A mixture of 0.50 g of 6-phenyl-4-methyl-2,4-diazatricyclo-[5.2.1.0^{2,6}]deca-3,5-dione (IVb-H_2) and 0.6 g (11 mmol) of potassium hydroxide in 20 ml of water was heated at 150° for 2 hr in a bomb. The reaction mixture was extracted with ether and the ethereal solution dried over KOH and evaporated. Examination of the residue by tlc showed a major product in addition to small amounts of starting material. The product's nmr spectrum ($CDCl_3$) had absorption at δ 1.53 (m, ~6), 2.3 (m, 1), 2.78 (d, J = 5 Hz, $NHCH_3$), 3.28 (m, 1), 3.58 (m, 1), 7.36 (m, 5), and 8.1 (br, NHCO). The mass spectrum (70 eV) had *m/e* 230 (0.2; pp), 229 (0.2), 172 (100), 144 (58), 143 (11), 115 (5), 104 (11), 91 (3), and 77 (3), among others. The spectral results indicate partial hydrolysis of the hydantoin and formation of 3-(N-methylcarbamido)-3-phenyl-2-azabicyclo[2.2.1]heptane.

Anal. Calcd for $C_{14}H_{19}N_3O$: C, 73.01; H, 7.88; N, 12.16; O, 6.95. Found: C, 72.69; H, 8.03; N, 12.28; O, 6.99.

Attempts to further hydrolyze the product with aqueous base were unsuccessful; intractable tars were formed. Reaction of IVb-H_2 with aqueous barium hydroxide at 100–150° or with ethylene glycol–potassium hydroxide afforded identical results.

Attempted Preparation of XX.—Under rigorously moisture-free conditions, 2.0 g of carbobenzyloxyphenylglycine (7 mmol) and 1.5 g (7 mmol) of PCl_5 were allowed to react in ether for 40 min at 0°.[42] The reaction mixture was then decanted and the solvent removed *in vacuo*, affording a residue which melted at around room temperature. The residue was dissolved in 20 ml of acetonitrile and then treated with 0.88 g (8 mmol) of *t*-butyl hypochlorite in 5 ml of CH_3CN and stirred overnight. The solvents were removed *in vacuo;* the residue was dissolved in 10 ml of dry benzene and added to 1 ml of cyclopentadiene and 1.1 ml (8 mmol) of triethylamine in benzene. After 3 hr the reaction mixture was poured into ice. Work-up by ether extraction followed by removal of volatiles *in vacuo* afforded an oily residue which was examined by tlc and nmr. The residue contained no adducts of cyclopentadiene and XX or hydrolysis products thereof.

When the chlorination was carried out in *t*-BuOH, polymerization of the Leuch's anhydride was observed.

Attempted Reaction of Ib with Cyclohexene.—A solution of 0.100 g (0.53 mmol) of Ib and 1 ml of cyclohexene (freshly distilled from $LiAlH_4$) in 10 ml of benzene was stirred for 16 hr at 25°. Examination of the infrared spectra of the solution showed that the imine absorptions at 1590 and 1560 cm^{-1} were undiminished. Heating for 60 hr at reflux also failed to effect reaction; the concentration of Ib was unchanged. Examination of the reaction mixture by tlc did not reveal the presence of any products.

Reaction of Ib with 3-Phenyl-4,5,5-trimethylisopyrazole.—A solution of 0.100 g of 3-phenyl-4,5,5-trimethylisopyrazole in 5 ml of benzene was heated at 55°. After 2 hr the reaction mixture contained a new component, on the basis of tlc. The reaction was complete after 16 hr and a crystalline material was present in the flask. Removal of the solvent *in vacuo* and recrystallization of the total residue afforded 0.156 g of colorless crystals, mp 208.5–210°. The structure XIIb was assigned from elemental and spectral analyses (Table II).

Attempted Reaction of Ib with 3,5-Diphenyl-4,4-dimethylisopyrazole.—A solution of 0.100 g (0.053 mmol) of Ib and 0.125 g (0.50 mmol) of 3,5-diphenyl-4,4-dimethylisopyrazole was heated for 72 hr at 60°. Careful examination of the reaction mixture by tlc and infrared spectroscopy (benzene–2-propanol, 9:1) indicated that no reaction had occurred.

Photochemical Reaction of Ib with Tetramethylethylene.—A solution of Ib (prepared from 0.3 g of IIb) and 5 ml of tetramethylethylene (purified by passage through active alumina) in 10 ml of benzene in a quartz tube was irradiated at 10° with an Hanovia high-pressure mercury lamp. The reaction was complete within 12 hr. Examination of the crude reaction mixture by tlc (silica gel; chloroform–methanol, 9:1) revealed a major product with an R_f greater than that of starting material. Column chromatography on Florisil afforded 0.205 g of viscous oil homogeneous by tlc. Fractional crystallization from chloroform–hexane afforded 0.065 g of crystalline material, mp 195–198°. Two recrystallizations from chloroform–hexane gave colorless crystals, mp 206–208°, which were identified by nmr spectroscopy (Table II) as 5-(1,1,2-trimethylprop-2-enyl)-5-phenyl-3-methylhydantoin (XIIIb). The mother liquors could not be induced to crystallize; the nmr spectrum ($CDCl_3$) had absorptions at δ 1.25, 1.40, 1.55, and 2.97 and 7.1–7.8, in addition to bands due to XIIIb.

A control reaction run with identical concentrations of the reactants but in the dark (16 hr at 25°) did not afford an observable concentration of product(s).

Reaction of Ic with Methanol.—A solution of 0.025 g (0.13 mmol) of sublimed Ib in 350 ml of benzene-d_6 was placed in an nmr tube. The solution was then treated with 0.20 ml of methanol and the reaction followed in the nmr cavity (39°). Within minutes two new singlets (other than those for CH_3OH) appeared; one was 2.5 Hz above the CH_3OH and the other was 2 Hz to higher field than the N–CH_3 absorption of Ib. The reaction was complete within 30 min. Removal of the solvent *in vacuo* and crystallization from ether–hexane afforded colorless crystals, mp 134.5–136°. The product was identified as 5-methoxy-5-phenyl-3-methylhydantoin (XIVb).

Registry No.—Ib, 25370-99-4; IIb, 6846-11-3; IIIb, 25371-01-1; IIIc, 25371-02-2; IVa, 25336-83-8; IVb, 25371-03-3; IVb (dihydro deriv), 25371-04-4; IVc, 25371-05-5; Vb, 25336-84-9; Vc, 25371-06-6; VIb, 25371-07-7; VIIb, 25371-08-8; VIIIb, 25371-09-9; VIIIc, 25371-10-2; Xb, 25371-11-3; XIIb, 25371-12-4; XIIb-d_3, 25371-13-5; XIIIb, 25371-14-6; XIVb, 25371-15-7; 3-phenyl-2-azanapthoquinone, 23994-23-2; 5-benzylidenehydantoin, 3775-01-7; 3-(N-methylcarbamido)-3-phenyl-2-azabicyclo[2.2.1]heptane, 25371-18-0; 6-phenyl-4-methyl-2,4-diazatricyclo[5.2.1.0^{2,6}]deca-3,5-dione, 25371-19-1; 6-phenyl-4-methyl-2,4-diazatricyclo[5.2.2.0^{2,6}]undec-3,5-dione, 25371-20-4.

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[42] M. Bergmann, L. Zervas, and W. F. Ross, *J. Biol. Chem.*, **111**, 245 (1935).